PRELIMINARY SMALL-SCALE COMBUSTION TESTS OF COAL LIQUIDS

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1.0 INTRODUCTION

Because of recent intense concern for environmental conservation, air pollutants which originate from combustion sources have attracted a great deal of attention, including sulfur oxides, nitrogen oxides (NO_x), and smoke particulates. Emission factors for stationary sources have been determined which relate the rate of pollutant emission to the types of boilers and furnaces and grades of fuel oils and other fuels.[1] Studies have demonstrated that NO_x emissions arise from two sources: (1) molecular nitrogen in the combustion air is oxidized via a thermal process to form "thermal NO_x"; and (2) nitrogen which is chemically bound in the fuel is converted to "fuel NO_x".[2,3,4] The most effective approach to eliminating NO_x emissions from combustion sources is the modification of the combustion process. Several combustion modification techniques have been developed to combat NO_x emissions, and staged combustion has been shown to be the most effective technique for the suppression of the oxidation of fuel nitrogen.[5,6] The smoking tendencies of fuel oils have been related to their API gravity and other properties.[1,7]

The growing imbalance between energy consumption and fuel production has created a need to supplement petroleum-derived fuels by the conversion of coal and other fossil fuel forms into liquid fuels. Studies by many organizations, including the Gulf Oil Corporation, have shown that low severity processing is sufficient to convert coal to a low sulfur liquid fuel. However, such liquids still differ from conventional petroleum-derived fuel oils in the same viscosity range; the coal liquids contain more nitrogen and aromatic compounds, being hydrogen deficient. As a result, the combustion of such liquids can be expected to produce greater emissions of NO_x and smoke and will require upgrading to produce suitable fuel products.

In order to obtain more information about the relationships between coal liquid composition and combustion emissions, we have submitted several coal liquids to the combustion tests to be described in this paper. In these tests a modified one-gph (3.8 dm^3 h) residential boiler was used, which required relatively small samples; the coal liquids were tested as produced and were in the quality range of a No. 4 fuel oil. Thus, these tests are preliminary in nature, and neither the boiler nor the liquids used are intended to represent future commercial equipment or fuel products. The results of these tests of coal liquids are instead to be interpreted by referring to some tests of conventional petroleum-derived fuel oils in the same boiler, which served to "calibrate" it. Some operating parameters of the burners and boiler were also varied to further establish their role in the combustion behavior of the coal liquids.

2. EXPERIMENTAL

2.1 EQUIPMENT AND PROCEDURES

The structure of the test boiler and associated equipment used is shown in Figure 1. The burner was fired horizontally into a firebrick-lined combustion chamber 38cm (15 in.) long, 28cm (11 in.) wide, and 35.5cm (14 in.) high; the flame gases then passed upward into the boiler section, where they were cooled to 230-290°C (450-550°F). Gases were sampled from the flue immediately above the boiler section, and

were delivered through 6.25mm O.D. stainless steel tubing to an ice bath and a train of continuous analyzers for NO_x (electrochemical or chemiluminescent), CO_2 and CO (NDIR), and O_2. Instrument accuracy was verified with Orsat readings for CO_2 and CO, and by comparison with combustion stoichiometric calculations. A Bacharach smoke number sampler (ASTM D 2156) was also positioned in the flue; smoke filter discs were read photometrically. The low velocity of the flue gases made isokinetic sampling impractical.

A modified residential "gun-type" burner was used, which had a motor-driven fan. The small orifice of the pressure-atomizing nozzle tended to become plugged by the coal liquids; and it was necessary to substitute an air-atomizing nozzle, which had no small orifices. This burner was also equipped with an efficient flame retention head, which was so positioned that all the combustion air emerged through it into the combustion chamber. Although this produced a high swirl and turbulence in the flame, it permitted measurements at low excess air levels without the formation of excessive smoke, which would tend to degrade the reliability of the flue gas analysis instruments. (The behavior of other burners with less air turbulence was also ascertained; these are described in Section 3.2) A further advantage of the air-atomizing nozzle (compared to pressure-atomizing nozzles) is the independent variability of fuel flow (which was controlled by a peristaltic pump), atomizing pressure, and fuel viscosity.

In a typical run, the fuel flowrate was held constant at 3.8 dm^3/h (1.0 gph), and the combustion air input was varied. The atomizing air pressure was 34.4kPa (5 psi) unless otherwise noted. The boiler was fired initially with No. 2 fuel oil to bring the system to equilibrium before introducing samples. Periodically, the No. 2 oil was fed into the system to check instrumentation and to serve as a reference. During a run, the combustion air was varied and measurements of Smoke Number, CO, CO_2, O_2, NO_x, and unburned hydrocarbon were taken. At each change of the air gate opening of other operating variable, the excess air level was calculated in the conventional manner from the measured CO_2 and the C/H content of the test fuel.

In addition to the measured total concentrations of NO_x in the flue gas, a parameter of interest is the portion of the NO_x which originated from the fuel nitrogen and the fraction of the fuel nitrogen which was converted to NO_x (the remainder of the fuel nitrogen emerging as N_2). The concentration of thermal-NO_x in the flue gases from the combustion of the test fuel was assumed to be the same as that measured in the combustion of No. 2 fuel oil, and was subtracted from the total value to obtain the fuel-NO_x concentration. (Two slight differences between the combustion of No. 2 fuel oil and of coal liquids which are neglected in this procedure are the different volumes of dry stack gases and the different flame temperatures, resulting from the use of the same volumetric fuel feed rate but different heat input rates. The resulting error is estimated to be less than 5%.) The fraction of fuel nitrogen converted to NO_x was obtained as the ratio of the observed fuel-NO_x concentration and the theoretical fuel-NO_x concentration computed for complete conversion by combustion stoichiometry. The nitrogen contents of the test fuels were determined by Kjeldahl analyses.

2.2 PROPERTIES OF FUELS

The properties of the fuels tested are listed in Table I. The coal liquids were produced in a bench-scale version of the Gulf Catalytic Coal Liquefaction process, which is based on the hydrogenation of a pulverized coal-solvent slurry. These liquids contained less than 0.1% sulfur. Samples F1 and F2 are filtered full boiling range process effluents; they were produced from western subbituminous and Pittsburgh Seam bituminous coals, respectively. These full-range liquids contained 0.5% nitrogen, and their viscosities were in the range of No. 4 or No. 5 fuel oils. Coal liquid "D" was a 130-350°C (270-670°F) distillate obtained from the full-range liquid F1; it contained 0.31% nitrogen and its viscosity was near that of No. 2 fuel oil.

3. RESULTS AND DISCUSSION

3.1 EMISSIONS FROM COAL LIQUIDS

Emissions of sulfur dioxide were very low because of the low sulfur content of these liquids. The concentrations of carbon monoxide and hydrocarbons in the flue gases were less than 5 ppm except at times when the smoke number exceeded eight. The smoke data are presented in Section 3.1.3; these coal liquids produced much less smoke than that which is encountered while burning typical petroleum-derived fuel oils having such low API gravities (7-14°API). When the excess air was greater than 25%, a relatively low air requirement, the smoke from the distillate and full-range coal liquids was within the limits corresponding (respectively) to home furnaces and industrial uses. The only emission which seemed to be problematic was NO_x.

3.1.1 Conversion of Fuel-Bound Nitrogen

The NO_x concentrations in the flue gas measured in the tests of the coal liquids in the air-atomizing test burner are shown in Figure 2. The distillate produced between 250 and 300 ppm of NO_x, and the full-range liquids produced between 300 and 400 ppm of NO_x. The emissions from No. 2 fuel oil are also shown. The concentration of NO_x in the flue gas did not vary greatly with excess air, but correction for dilution by excess air shows (Figure 3) that the amount of NO_x emitted from the burning of coal liquids increased with excess air; this was due to increased oxidation of the fuel-bound nitrogen. The amount of thermal NO_x produced by the No. 2 fuel oil decreased with increasing excess air, due to cooling of the flame by the additional air.

The effects of the nitrogen content of the fuels and of the excess air levels in the tests can best be seen in Figure 4, which presents the fraction of fuel nitrogen converted to NO_x as a function of the excess air level. We first compare the behavior of the coal liquids and petroleum fuels when the excess air was 25%. Thirty-two and forty percent of the nitrogen in the full-range coal liquids was converted to NO_x. These conversion values are close to those for 0.5% nitrogen petroleum oils reported by Turner and Siegmund;[3] in that study, a 10-gph boiler was used, which contained an insulation-lined combustion chamber and an air-atomizing nozzle. The fuel nitrogen conversion exhibited by the distillate coal liquid in our tests was 52%, which is higher than that of the full-range liquids; this value is also close to that of a petroleum fuel oil containing 0.3% nitrogen, observed by Turner and Siegmund.[3] These values for fuel nitrogen conversion in the coal liquids are also consistent with the observation by others that more of the fuel nitrogen is converted in less nitrogen-rich fuels.[2,3,6] It is possible that the test unit used in this study and in the large unit reported in Reference 3 involves flames which are similar in aspects that affect fuel nitrogen conversion; if so, one can conclude that the NO_x emissions from coal liquids will generally resemble that from petroluem fuel oils in such boilers. Observations of the effects of burner operating parameters are described in Section 3.2.

Thus, the distillate coal liquid contained only 60% as much nitrogen as the full-range coal liquids, but it yielded nearly as much NO_x in combustion, as a result of the higher fuel nitrogen conversion associated with its lower nitrogen concentration.

In addition to the effect of the nitrogen concentration on the conversion levels, other differences between the distillate and full-range liquids may have influenced the nitrogen conversions in these liquids. The viscosity of the full-range liquid was four times that of the distillate, and from a correlation for pneumatic atomizers,[8] it was estimated that the mass mean diameter of the droplets in the filtrate spray was twice that of the distillate droplets. Furthermore, the droplets of the full-range liquid probably volatilized in the flame more slowly than those of the distillate.

There are also a few indications of effects of the volatility and composition of the nitrogen compounds in the fuels. Approximately one-half of the nitrogen compounds in the full-range liquid F1 boiled above 350°C (670°F), in contrast to the nitrogeneous components of the distillate, which of course all boiled below that temperature. Tests of pyridine-doped No. 2 fuel oil in the test burner (curve "10" in Figure 7) also indicate that the pyridine was more extensively oxidized than were the nitrogen compounds in the distillate coal liquid. [The conversion of the 0.5% N oil (as pyridine) was close to the nitrogen conversion level (52% at 25% excess air) of the distillate coal liquid (which contained 0.3% nitrogen), and the conversion of 0.3% N oil (as pyridine) would then definitely exceed 52%.] Finally, in three of the burners employed in tests described in Section 3.2, the conversion of piperidine in No. 2 fuel oil was 10-15% greater than the conversion of pyridine; the dopant level was 0.50% N in both cases, and this difference occurred only between 50% and 100% excess air.

3.1.2 Effect of Excess Air

The major operating parameter which affects combustion emissions is the excess air level. In tests of the coal liquids in the test burner, between 70% and 80% of the fuel nitrogen in all the coal liquids was converted to NO_x at very high excess air levels. The fuel nitrogen conversion exhibited by the distillate liquid decreased regularly to 40% as the excess air level was reduced to 6%. These conversion levels are close to those observed by Turner and Siegmund.[3] They also found that the conversion continued to decrease as the air feed was reduced below stoichiometric values, in a simulation of the first stage of staged combustion; this accounted for the success of this technique. The conversion of the fuel nitrogen in the full-range coal liquids exhibited a similar response to decreasing excess air, although in the lower excess air range, its decrease appears to be unusually rapid. Others have also noted dramatic decreases in conversion with decreasing excess air.[5] Thus, staged combustion may serve to limit the NO_x emissions arising from the nitrogen in coal liquids. This technique is also likely to be more effective in larger furnaces whose residence time is longer than that of the test unit used here. However, staged combustion is limited by the soot formed in the fuel-rich first stage, and this limitation will become problematic with coal liquids.

3.1.3 Smoke Emissions

The smoke measurements made during these tests of the coal liquids in the test burner are shown in Figure 5. Data are also included from tests of anthracene oil and No. 4 fuel oil [the latter at 138kPa (20 psi) atomizing air pressure]. No. 2 fuel oil gave no smoke when the excess air exceeded 12%. When the excess air was greater than 25%, the smoke from the distillate coal liquid was less than ASTM smoke No. 1 (a typical performance requirement for a home furnace) and the smoke from the full-range liquids was less than approximately a Ringelman number one, which is a common limit for industrial furnaces. This is a relatively low air requirement. When the excess air was increased above 50%, the smoke from the distillate fuels (including anthracene oil) decreased to less than ASTM smoke No. 1; in contrast, the residual fuels (the full-range coal liquids and the No. 4 fuel oil) produced moderately persistent smoke.

There is a relationship between the smoking tendencies of these fuels and some of their compositional properties. The most influential of these properties is apparently the non-volatile content of the full-range fuels, whose persistent smoking places them in a separate group from the distillate fuels. Further comparisons of smoke formation from full-range coal liquids and from petroleum residual fuels are needed and may be made possible by using a variable fuel preheater in the test burner. The API gravity of the distillate fuels is closely related to their tendency to form soot in the low excess air range. Viscosities and carbon numbers do not seem

to bear any regular relation to the smoking tendencies of this set of fuels, although these properties are also important.

In order to obtain further information about the effect of the aromatic content of fuels on their smoking tendencies, a middle distillate cycle oil was tested. It resembled the distillate coal liquid, since its API gravity was 15.3; but it did not plug pressure-atomizing nozzles, permitting the use of a conventional but efficient home furnace burner. No. 2 fuel oil was also burned for comparison. The No. 2 fuel oil required 17% excess air to limit the smoke from its combustion to a number one spot; and the cycle oil required a moderate increase in excess air, to 27%, to reduce its smoke to this limit.

3.2 EFFECT OF BURNER DESIGN ON EMISSIONS

As we have described, the combustion of the coal liquids in the residential-size test burner produced fuel nitrogen conversion levels which were close to the conversions reported for residual petroleum fuel oils burned in somewhat larger units. These latter furnaces had air-atomizing nozzles; and in comparison with residential burners, they had longer residence times and higher flame temperatures. In contrast, tests by Martin[2] in a representative residential furnace produced fuel nitrogen conversions which were generally 50% lower then those observed in our modified residential test furnace and in the larger units mentioned above. A pressure-atomizing nozzle was employed by Martin to burn a series of No. 2 fuel oils doped with pyridine and other nitrogen compounds; this unit had a high tendency to form smoke.

On the other hand, much greater fuel nitrogen conversion has been observed in small combustors in which very high combustion intensities were produced by accelerated mixing of combustion air and fuel, and also by the fine atomization of the oil.[4,9] In such units between 50% and 100% of the fuel nitrogen was converted to NO_x. In order to relate our results to these various studies, several burners were assembled having various air handling parts which varied the air mixing rate over a wide range; these burners were used in a series of tests with No. 2 fuel oil doped with pyridine at the level of 0.50% nitrogen. Since the smoke-forming tendency of such burners decreases with an increasing air fuel mixing rate, the smoke number curve of each burner was used to empirically characterize its mixing rate as shown in Figure 6. Each burner is designated by the excess air level which it required to reduce the smoke to a number one spot; for example, the test burner used in the coal liquids test required only 10% excess air, while the least efficient residential burner required 120% excess air. Pressure-atomizing nozzles were employed in all burners except Unit "10", and the droplets produced by the former were probably several times larger than those produced by the air-atomizing nozzle in Unit 10. Burners 40A, 40B, and 120 were fired in the same test boiler as Unit 10, but had various air handling parts and/or flame retention heads. Curve "75" is plotted from data obtained[10] from the test furnace employed by Martin and Berkau in the tests of pyridine-doped No. 2 fuel oil which we cited above.[2]

Each of these burners was used to fire No. 2 fuel oil which contained 0.5% nitrogen as pyridine; Figure 7 displays the fuel nitrogen conversion observed in each burner plotted as a function of excess air. At any excess air value, the fuel nitrogen conversion was greater in burners having lower smoking tendencies or faster air-fuel mixing. For example, at 50% excess air, Burner 120, which produced the most smoke, converted only 35% of the fuel nitrogen to NO_x. In contrast, in Unit 10, the fuel nitrogen conversion to NO_x was 70%.

4.0 CONCLUSIONS

In the following, we summarize the observations made with the particular fuels and boiler used here, and note some implications of these results.

1. Generally, the combustion of the coal liquids produced negligible amounts of sulfur oxides (because of their low sulfur content) and CO and hydrocarbons. The amount of smoke from the combustion of the distillate and the full-range liquids was less than the typical limits for (respectively) home furnaces and for industrial units. Only the NO_x emissions were potentially problematic. This problem can be solved with the removal of nitrogen from some coal liquids by upgrading; the minimum processing requirements for this are now being ascertained.

2. The coal liquids tested contained 0.3% and 0.5% nitrogen, and the concentration of NO_x in the flue gas resulting from their combustion ranged between 240 and 400 ppm. The behavior of the coal liquids in the test burner used here was similar to that observed by Turner and Siegmund in their tests of petroleum residual oils in a 10-gph boiler. At 25% excess air, 35% to 50% of the fuel-bound nitrogen was converted to NO_x. Although the nitrogen content of the distillate coal liquid was 40% less than that of the full-range liquid, NO_x emissions from the former were not appreciably reduced. The reduction in NO_x emissions with decreasing excess air suggests that staged combustion will be effective when applied to coal liquids combustion, although smoke formation may then be problematic.

3. Pyridine-doped No. 2 fuel oil exhibited more extensive conversion to NO_x than did the distillate coal liquid, probably due to the lower volatility of the nitrogen content of the latter. Piperidine appeared to exhibit slightly higher conversion than did pyridine, at high excess air levels. There was little difference between the emissions from the combustion of full-range liquids derived from bituminous and sub-bituminous coal.

4. Tests of pyridine-doped No. 2 fuel oil in a series of modified burners showed that as the fuel-air mixing rate was increased and smoke formation decreased, the conversion of fuel nitrogen was doubled. The fuel-air mixing rate in the test burner used in the coal liquids tests was greater than that in conventional home furnace burners.

In conclusion, these tests of coal liquids illustrate how several fuel properties and equipment and operating parameters affect the emissions of NO_x and smoke from these fuels. These effects are similar to those noted in others' observations of the combustion of petroleum fuel oils, although more definitive testing is indicated.

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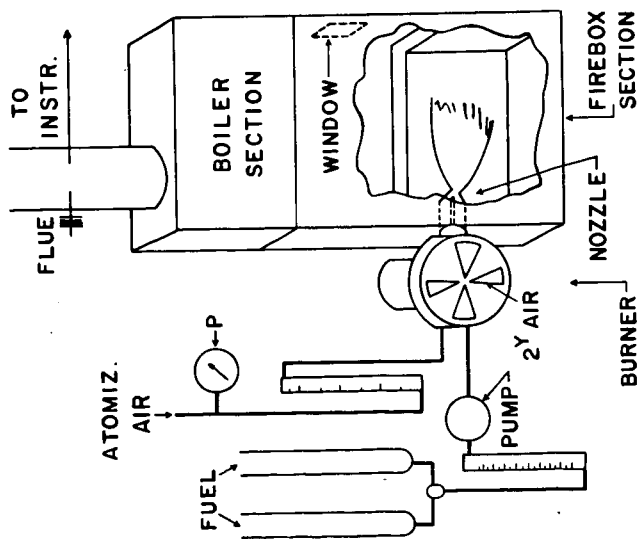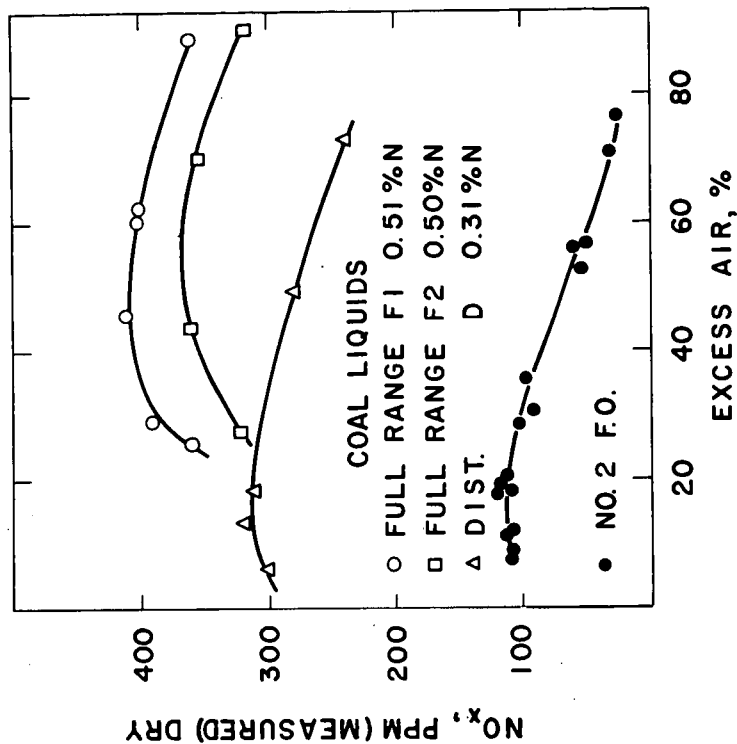
FIGURE 2

MEASURED NOx CONC.

COAL LIQUIDS

○ FULL RANGE F1 0.51%N
□ FULL RANGE F2 0.50%N
△ DIST.   D 0.31%N

● NO. 2 F.O.

NOx, PPM (MEASURED) DRY

EXCESS AIR, %

FIGURE 1

RESIDENTIAL BOILER AND
ASSOCIATED EQUIPMENT

TO INSTR.

BOILER SECTION

WINDOW

FIREBOX SECTION

NOZZLE

BURNER

2Y AIR

PUMP

FLUE

P

ATOMIZ. AIR
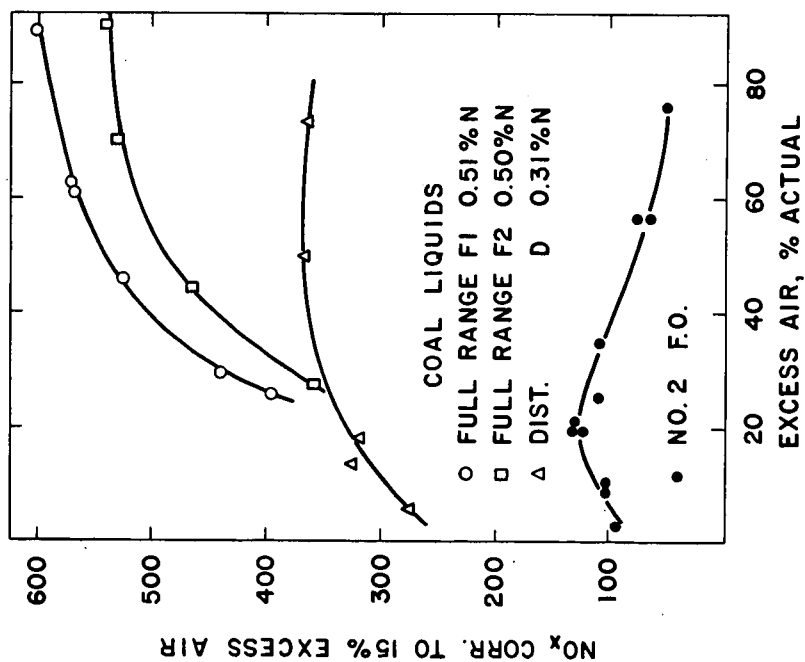
FUEL

FIGURE 4
CONVERSION OF FUEL-N

COAL LIQUIDS
○ FULL RANGE F1 0.51%N
□ FULL RANGE F2 0.50%N
△ DIST.   D   0.30%N

× RESID. F.O., REF. 3 0.3%N
+ RESID. F.O., REF. 3 0.5%N

% OF FUEL-N CONVERTED TO NOₓ

EXCESS AIR, %

FIGURE 3
AMOUNT OF NOₓ

COAL LIQUIDS
○ FULL RANGE F1 0.51%N
□ FULL RANGE F2 0.50%N
△ DIST.   D   0.31%N

● NO. 2 F.O.

NOₓ CORR. TO 15% EXCESS AIR

EXCESS AIR, % ACTUAL
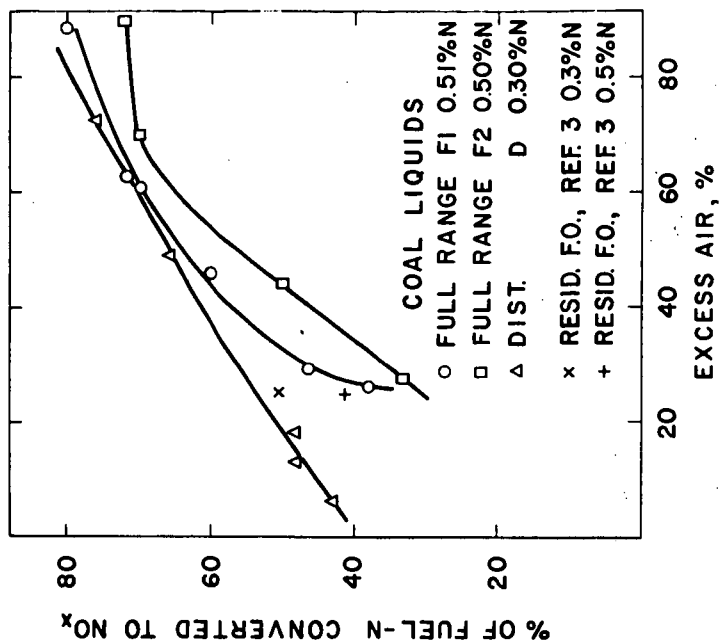
FIGURE 5
SMOKE FROM COAL LIQUIDS AND OTHER FUELS
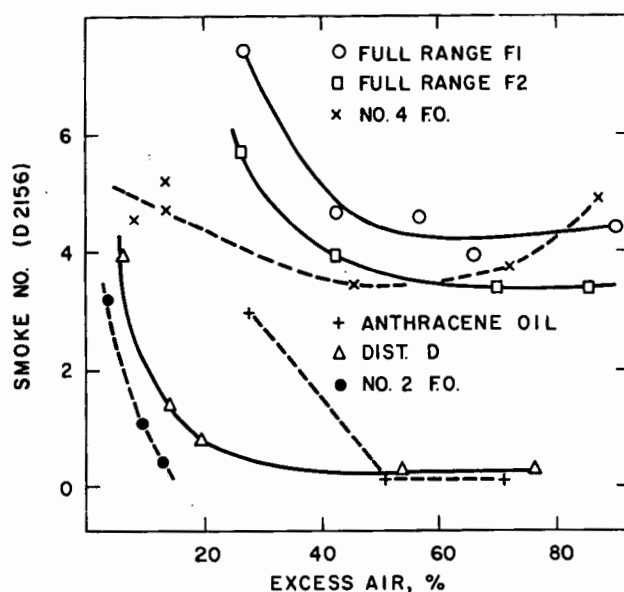
FIGURE 6
SMOKE FROM VARIETY OF BURNERS

BURNER 10: AIR ATOMIZING NOZZLE – I GPH
OTHER BURNERS: PRESSURE ATOMIZING NOZZLES – I GPH
BURNER 75: WASSER, ET. AL., REF. 10, 0.75 GPH
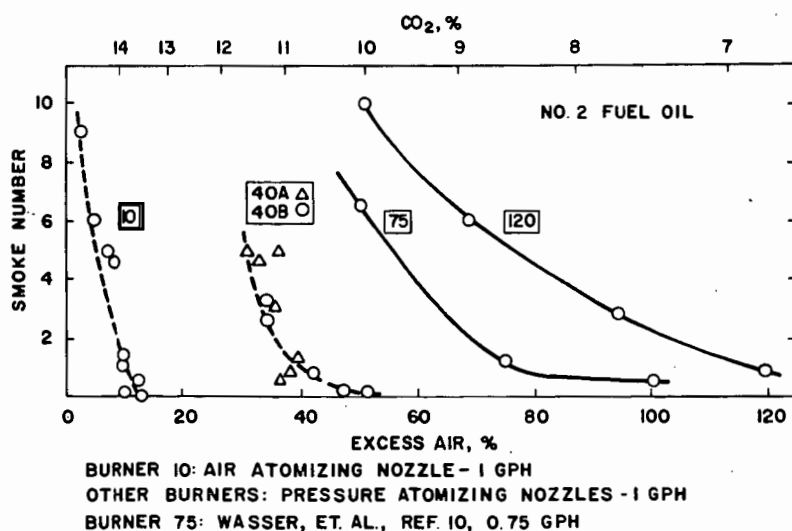
FIGURE 7
EFFECT OF BURNERS ON FUEL-N CONVERSION

214
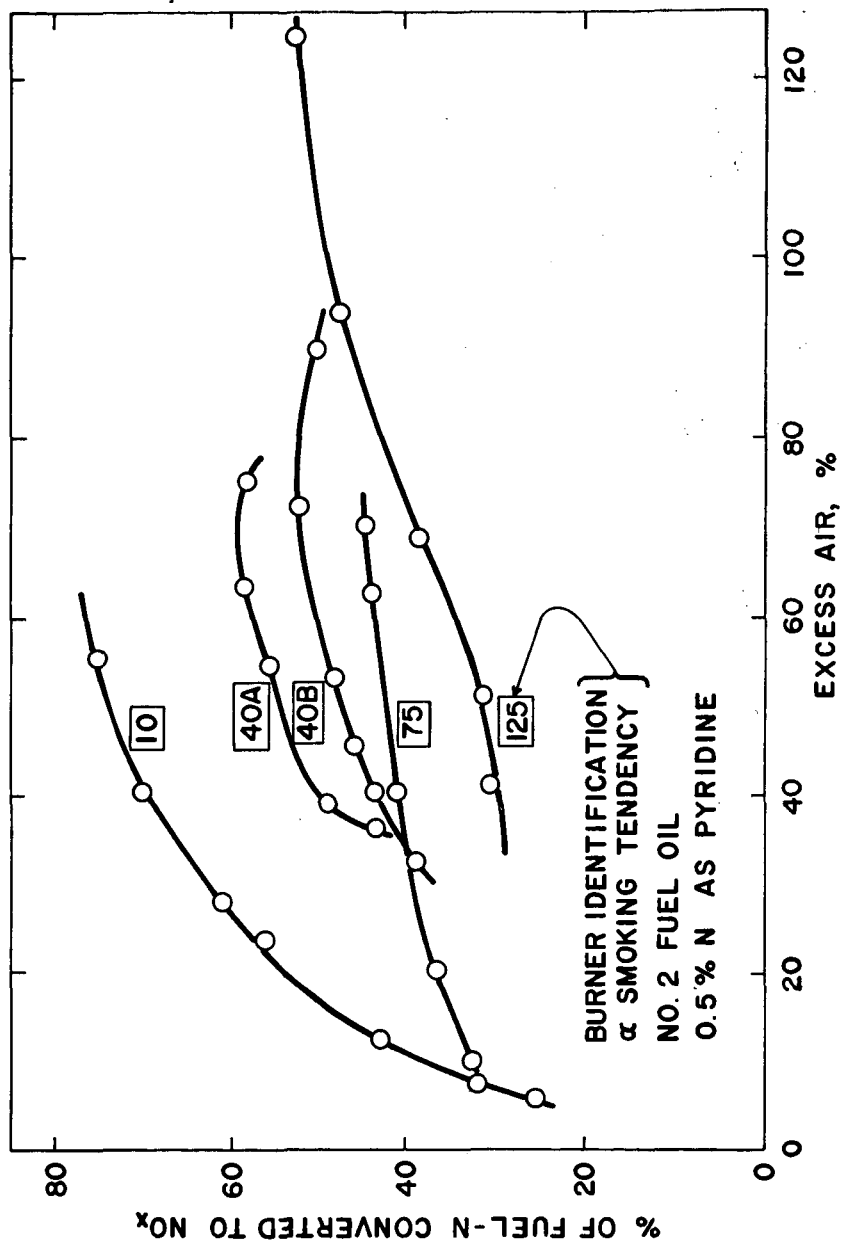
Table I

PROPERTIES OF FUELS TESTED

| | ←——————Coal Liquids——————→ | | | | | | |
	Distillate D	←—Full-Range—→ F1	F2	Anthracene Oil	Cycle Oil	No. 2 Fuel Oil	No. 4 Fuel Oil
Gravity °API	14.1	7.0	10.4	-	15.3	34.5	28.3
Density, 15°C (kg/l)	0.9730	1.0217	0.9970	-	0.9638	0.8524	0.8854
Ash %w	.0030	0.010	.013	.002	-	-	-
Carbon %w	89.56	89.93	89.0	91.02	90.7	86.9	86.41
Hydrogen %w	9.54	8.84	9.44	5.90	9.3	13.1	12.36
Nitrogen %w	0.31	0.51	0.50	0.98	-	0.01	-
Sulfur %w	.04	0.07	-	0.58	0.50	0.10	-
Dist. Range, °C (°F)	130-364 (266-688)	-	-	>200 (>392)	204-338 (400-640)	182-338 (360-640)	-